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Theoretical study of resonance formation in microhydrated molecules (II): thymine-(H₂O)_n, n=1,2,3,5

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We have investigated the effect of microsolvation on the low-lying pure shape π^* resonances of thymine. Static-Exchange R-matrix calculations for elastic electron scattering from microhydrated thymine, i.e. Thy-(H₂O)_n with n=1,2,3,5 are discussed. We look at the additive effect of water molecules hydrogen-bonding to thymine. The results for Thy-(H₂O)₅ show that both π^* resonances appear at lower energy in the cluster than in isolated thymine, but that the energy shift is different for each resonance. We discuss how our results could help explain the quenching of hydrogen loss in dissociative electron attachment of microhydrated thymine recently recorded experimentally.

PACS numbers: Valid PACS appear here

Keywords: electron scattering, resonances, mycrohydration, nucleobase

INTRODUCTION

Over the last two decades or so, one of the main focuses of electron-molecule collision studies has been the interaction with the nucleobases¹. The interest stems from the importance that processes induced by low energy electrons, in particular dissociative electron attachment (DEA), have in biological radiation damage². In addition to nucleobases, other DNA constituents and simpler 'model' molecules (e.g. pyrimidine, tetrahydrofuran), have been subject to both theoretical and experimental gas phase studies. Work on oligonucleotides has also been performed, for example, investigating the effect that the base sequence has on the damage (DNA strand breaks)³.

The attachment energies of electrons to the nucleobases in the gas phase were first determined in 1998 by Aflatooni *et al.*⁴ in an electron transmission spectroscopy (ETS) experiment. Since then, several groups have measured yields of anionic fragments of thymine and uracil produced through DEA^{5–13}.

Theoretically, low energy electron collisions with thymine and/or uracil molecules have been studied with the Schwinger Multichannel method^{14–16}, using a single-centre expansion^{17–19}, with the R-matrix eigenchannel method²⁰ and with the R-matrix method^{21–23}. All these studies looked at shape resonances, and those using the R-matrix method also investigated core-excited ones. None of them, however, have considered the effect of the environment (the cell is a condensed environment where all molecules are surrounded by other molecules, mainly water) in the collision process.

Clusters can be seen as systems that bridge the gap between the gas and the condensed phase. Therefore, the study of clusters of hydrated DNA constituents (i.e. clusters of a single nucleobase and a number of water molecules) can help us understand how the presence of water in the cell affects electron-induced damage. Experimentally, DEA to pure and hydrated clusters of pyrimidine was investigated²⁴: the measured anion yields were very different from gas-phase pyrimidine and also for the two types of clusters showing the strong effect of clusterization on DEA. Some computational work has been performed on electron scattering from dimers and trimers of small molecules and phenol (see Paper I²⁵). The current understating is that water hydrogen-bonded to a molecule will stabilize its resonances if it acts as a hydrogen donor and it will destabilize them if it acts as an acceptor; moreover, the effect of two water molecules will be approximately additive²⁶.

A handful of quantum chemistry studies on microsolvated nucleobases are available. Calculations of the ionization energies of microhydrated thymine²⁷ and the vertical detachment energies of microhydrated thymine, uracil and adenine-uracil base pairs^{28–30} have been performed. Calculations of cross sections for hydrogen detachment from uracil/thymine surrounded by five water molecules (in their model, these molecules are treated as interchangeable) have been carried out considering a single nuclear coordinate³¹. Smyth *et al.* used a non-local complex potential approach and multiple scattering theory (see their paper for details) to study the N₁-H fragmentation process for the optimized geometry of the cluster (shown in Figure 1); the method had been successfully applied to the study of dehydrogenation of gas phase uracil/thymine³². The required vertical electron attachment (VEA) energy was determined for the first π^* resonance using standard (bound state) computational chemistry techniques. This VEA was found to be smaller than that of the isolated molecule. This result is consistent with the approximate additivity of the hydration effect and the fact that three of the water molecules act as hydrogen donors and two as acceptors. The assumption was made that all resonances (in particular, the σ^* resonance involved in the DEA process they studied³²) were therefore stabilized by microhydration. Their calculations showed that the DEA cross section for hydrogen detachment is strongly enhanced by hydrogen-bonding to several water molecules.

Very recently, DEA in clusters of a single thymine or uracil molecule and a few water molecules for electron energies below 3.5 eV has been investigated³³. Strikingly, the signal for dehydrogenation completely disappears for both hydrated nucleobases. This result seems to be in contradiction with Smyth *et al.*'s theoretical outcome³¹. However, the possible explanation given by J. Kočíšek *et al.* is linked to a 'caging' effect that prevents the H atom from detaching.³³ This effect is not included in Smyth *et al.*'s calculations. It seems clear that further investigation of DEA from microhydrated uracil/thymine is required to understand the quenching of the dehydrogenation process.

This paper continues the work presented in Paper I²⁵. Here, we study the two lowest resonances in thymine for several geometries of the Thy-(H₂O)_n clusters with n=1,2,3,5. The methodology employed is the same: the R-matrix method, as implemented in the UKRmol+ suite, has been used to determine resonance characteristics at Static-Exchange (SE) and Static-Exchange + Polarization (SEP) levels. As explained in Paper I, SEP calculations provide less reliable resonance shifts because it is not currently possible to describe

polarization effects to the same accuracy in all calculations³⁴. In addition, we use the same distinction of direct and indirect effects of microhydration to investigate the effect of water on the resonances. A definition of these, and a description of the R-matrix method and the specific models used can be found in Paper I.

The aim of this paper is three-fold: (i) to confirm the approximate additivity of the hydration effect as established for simpler molecules and phenol^{26,35} for this nucleobase; (ii) determine whether this effect is quantitatively the same for different resonances of the target; (iii) compare the resonance parameters for Thy-(H₂O)₅ obtained from our scattering calculations with those used by Smyth *et al.* in their DEA calculation in order to shed light on the experimental results. We will also compare the results of thymine with those from pyridine in Paper I.

II. CHARACTERISTICS OF THE CALCULATION

Calculations have been performed for a number of geometries of the Thy-(H₂O)_n clusters with $n=1,2,3,5$. The optimized geometries of Thy-(H₂O)₅ and Thy-H₂O with water attaching to 3 different bonding sites were determined by Smyth *et al.*³¹: these were obtained from sophisticated DFT calculations. The other, non-optimized geometries, have been obtained from these (see below).

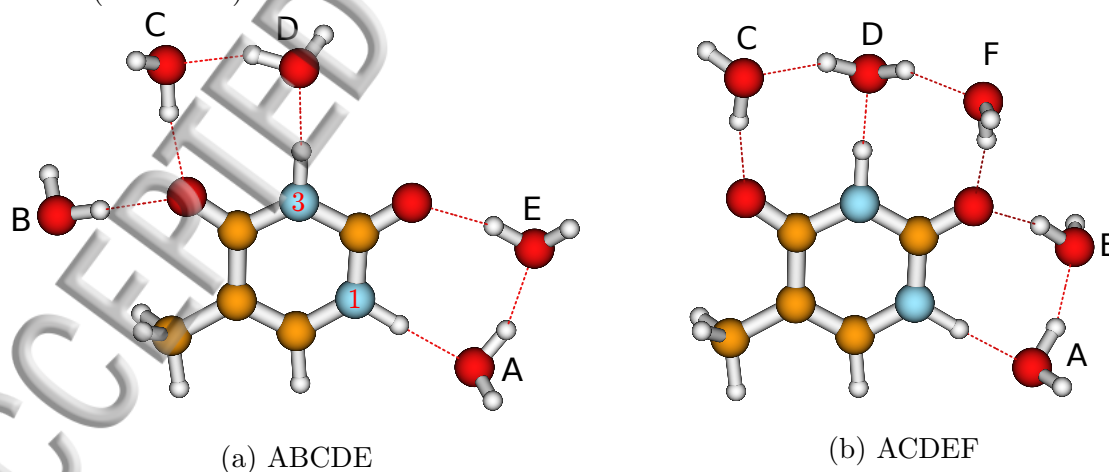


FIG. 1: Structure of Thy-(H₂O)₅ for the two different geometries studied in this work. (a) optimized geometry from Smyth *et al.*³¹; (b) alternative geometry used in some calculations. The labels of each water molecule in the geometry ABCDE are used throughout the text. The atoms N₁ and N₃ of thymine are indicated in the cluster ABCDE.

Figure 1(a) shows the optimized geometry for Thy-(H₂O)₅. Calculations were also performed for a slightly different geometry shown in Figure 1(b) to investigate how geometry changes affected the resonances. Note that the differences between these two geometries are small: the water molecule labelled 'B' in the optimized geometry is attached to the other Oxygen in thymine (but remains a hydrogen donor). This leads to some re-orientation of the other water molecules and some changes to the distance between them and thymine, but not changes to their bonding site; the geometry of the thymine molecule itself also changes slightly.

All calculations in this work have been performed using the cc-pVDZ basis set, proven to provide a reasonable description in more accurate calculations for thymine²². The target calculations were performed at Hartree-Fock level. The calculated ground state energy and dipole moment of all targets studied are collected in Table I. For the scattering calculations, an R-matrix radius $a = 18 a_0$ was chosen and partial waves up to $l_{max} = 6$ included; 10 virtual orbitals (v.o.) have been included in the calculations for all systems. (SEP calculations have been carried with 15 frozen and 18 active thymine orbitals).

In order to investigate the contribution of each water molecule to the changes in resonance position in Thy-(H₂O)₅, we looked at Thy-H₂O in a number of geometries. These geometries were generated by removing 4 water molecules from the ABCDE cluster. In addition, we performed calculations for optimized geometries of the Thy-H₂O cluster (the optimization leads to only three distinct clusters; for details, see *Smyth et al.*³¹). These are plotted in Figure 2: the geometries are labelled Aeq, Beq and Deq to indicate that in each of them the water binds to the same site as the A, B and D water molecules in Thy-(H₂O)₅ respectively. It can be seen, however, that these geometries are different to those corresponding to leaving the A, B or D water molecule in the Thy-(H₂O)₅ cluster: the relative orientation of the water molecule, and the distance to the ring, are different.

MOLDEN draws a red dashed line when a hydrogen bond is present in the system (it determines its presence by looking at geometrical parameters). The plots in Figure 2 do not indicate a hydrogen bond for clusters Aeq and Deq. In the original paper³¹, where DFT was used to determine the wave function for these systems, water is hydrogen-bonded to thymine for all these clusters. The lack of hydrogen bonds for Aeq and Deq in Figure 2 suggests these bonds are weaker in our Hartree-Fock calculation than in the DFT one. Nevertheless, we believe the effect on the resonances can be interpreted as being due to hydrogen-bonding.

System		E	μ
Thy	G1	-451.548	4.64
	G2	-451.542	4.92
	G3	-451.528	4.94
Thy-H ₂ O	A	-527.581	6.45
	B	-527.579	4.47
	C	-527.577	7.19
	D	-527.579	2.54
	E	-527.578	3.41
	Aeq	-527.591	3.93
	Beq	-527.584	3.67
	Deq	-527.588	4.95
Thy-(H ₂ O) ₂	AD	-603.618	4.04
	AE	-603.630	4.47
	BC	-603.612	6.21
	BD	-603.616	2.72
Thy-(H ₂ O) ₃	BCD	-679.663	3.35
	BCE	-679.647	4.63
Thy-(H ₂ O) ₅	ABCDE	-831.752	4.65
	ACDEF	-831.740	4.26

TABLE I: Ground state energy (E) in Hartree and dipole moment (μ) in Debye of isolated thymine and Thy-(H₂O)_n calculated in this work at Hartree-Fock level. G1: equilibrium geometry of isolated thymine in its ground state; G2: geometry of thymine in the optimized ABCDE cluster; G3: geometry of thymine in the ACDEF cluster. Aeq, Beq and Deq are optimized geometries³¹ but all others correspond to the removal of one or more water molecules from the ABCDE cluster.

III. RESULTS

As all pyrimidinic molecules (and pyridine), thymine possesses three low-lying π^* resonances: the two-lowest are pure shape and the third one is of mixed shape and core-excited

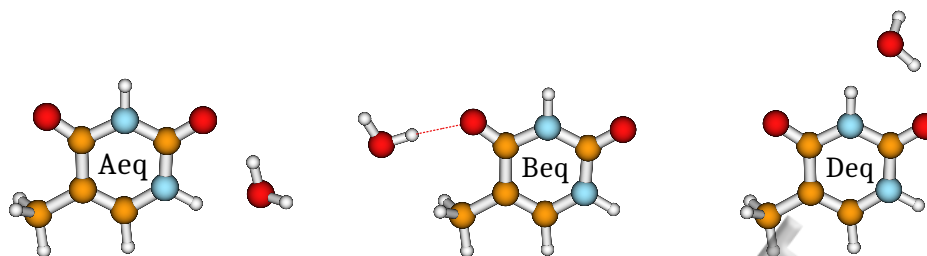


FIG. 2: Structure of the three optimized geometries of Thy-H₂O determined by *Smyth et al.*³¹. We have retained the labels A, B and D as the bonding-site for the water molecule in each of this optimized geometries is that of the A, B and D water molecules in Thy-(H₂O)₅. The relative orientation of water with respect to thymine, however, is different in all cases.

character²². Below, we focus mainly on the two pure shape π^* resonances and analyse how their positions are affected by water hydrogen-bonded to thymine. The concepts of indirect (i.e due to geometry changes) and direct (i.e. due to the presence of water) effects are used to interpret results.

A. Thymine-H₂O

The time-delay calculated at SE level for the Thy-H₂O clusters represented in Figure 2 is plotted in Figure 3 together with that for isolated thymine in its ground state equilibrium geometry (Thy G1). The geometry of thymine in these clusters is extremely similar to that of isolated thymine. Therefore, indirect effects are negligible for these systems and the total effect, observable in Figure 3, can be taken as identical to the direct effect. (We note that the Thy-H₂O geometries have been optimized using a more sophisticated calculation than that used to optimize the geometry of Pyr-H₂O in Paper I; indirect effects were not negligible in that case.)

Both resonances are stabilized for Beq, as expected since water acts as hydrogen donor. However, for clusters Aeq and Deq, the lower resonance is slightly destabilized and the higher one slightly stabilized. One can assume that water in these two geometries acts both as proton donor and proton acceptor (although in *Smyth et al.*'s work this is true for Aeq but not for Deq: Figure 3 in their paper³¹ shows two hydrogen bonds for Aeq only). The different behaviour of the first and second resonances can be understood analysing

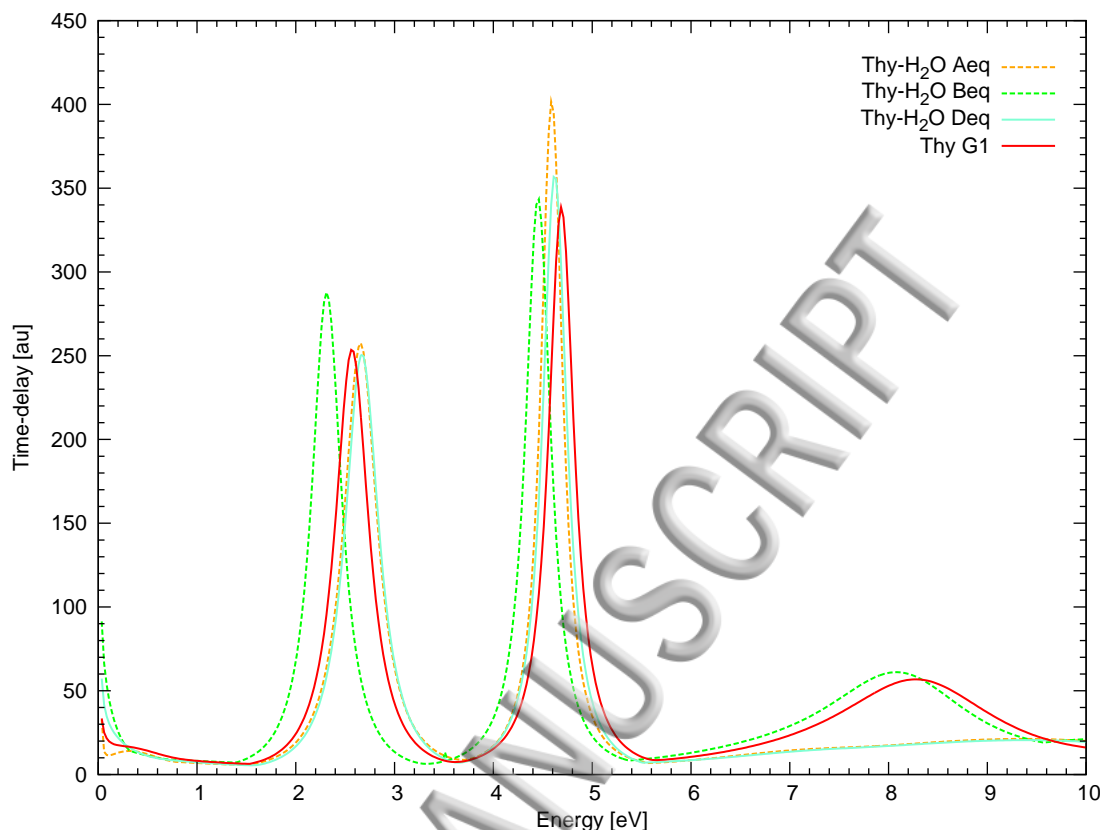


FIG. 3: Time-delay calculated at SE level with 10 v.o. for the three geometries of Thy-H₂O indicated in the figure and for isolated thymine in its equilibrium configuration (Thy G1). For geometries Aeq and Deq, the third resonance (of mixed shape-core-excited character) is not present as the third π^* orbital is not present amongst the 10 lowest energy v.o. that have been included in each calculation (this is also the case for other time-delays when the third resonance is not visible).

the orbitals into which the electron is trapped. Figure 4 shows the two lowest unoccupied π^* orbitals of thymine: one can see that for Aeq and Deq the first π^* orbital has low density close to the water, but has slightly more density nearer the oxygen than the hydrogen in the water molecule. Also, the distance between the oxygen in H₂O and the hydrogen in thymine is slightly shorter than between the hydrogen in H₂O and the oxygen in thymine. Therefore, we can say that water behaves more strongly as a proton acceptor than proton donor, explaining the destabilization of the first π^* resonance. The second π^* orbital has much more density close to hydrogen in H₂O than its oxygen; therefore, in this case, water behaves more as a proton donor than proton acceptor, stabilizing the second π^* resonance.

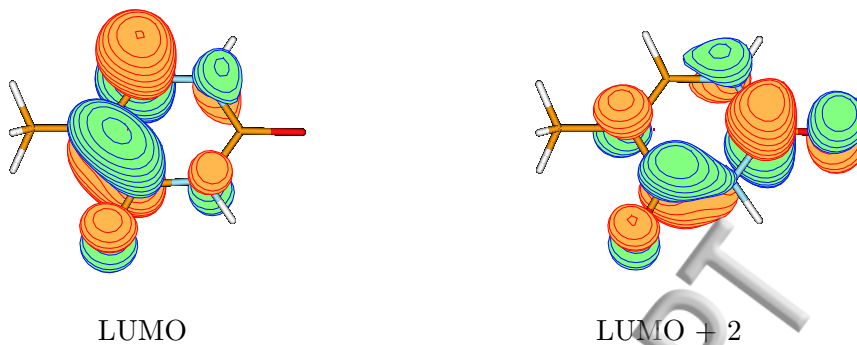


FIG. 4: The LUMO ($1\pi^*$) and LUMO + 2 ($2\pi^*$) of thymine in its ground state equilibrium geometry.

These results show that there are situations where water does not have the same effect on all resonances, particularly when it forms more than one hydrogen bond with the target molecule. It should be noted that in SEP calculations both resonances are either stabilized or destabilized. This probably means that the small effect due to the static and exchange potentials is overridden by (stabilizing) polarization effects

Smyth et al. find (in their bound state calculations) that the lower resonance is stabilized for all 3 geometries (with Beq providing the largest stabilization). Even in our SEP calculations the first π^* resonance is destabilized for Aeq and Deq (though this might be, of course, because of a better description of the polarizability of thymine than for Thy-H₂O, though this does not seem very likely since the spherical polarizability of water is around $10 a_0^3$ whereas that of thymine is around $70 a_0^3$).

In the case of Pyr-H₂O all shape resonances were stabilized but, we note, water formed a single bond with it and acted exclusively as a hydrogen donor.

B. Thymine-(H₂O)_n, n=2,3

In order to investigate how the effect of several water molecules hydrogen-bonding to thymine combine to affect the resonances, we have investigated several clusters in which two or three water molecules have been removed from Thy-(H₂O)₅ in the ABCDE geometry. Figure 5 shows the time-delay for two Thy-(H₂O)₂ clusters: one with the water molecules in the A and D positions (upper panel) and another with the water molecules in the A and E positions. Also shown in the panel are the time-delays for Thy-H₂O with water in the A,

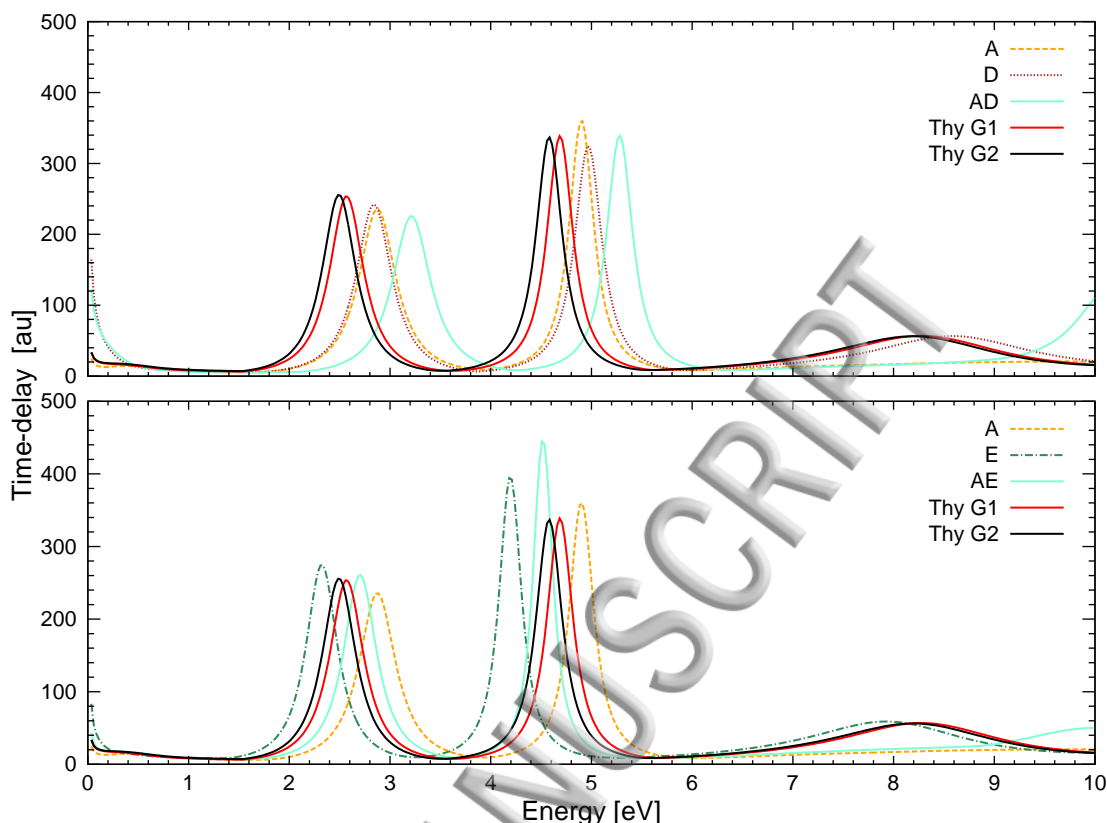


FIG. 5: Time-delay calculated at SE level with 10 v.o. for thymine in its equilibrium geometry (Thy G1) and the geometry it has in the ABCDE cluster (Thy G2) and Thy-(H₂O)_n, $n = 1, 2$ for the geometries indicated in the panels.

D or E position (note that these are not for the optimized geometries for which time-delays were presented in the previous section) and for isolated thymine in the geometry it has in the ABCDE cluster (Thy G2) and its equilibrium geometry (Thy G1). The results for Thy G2 are used to illustrate this indirect effects. The three visible resonances appear at very similar energies for Thy G1 and Thy G2: the indirect effects are small (but, unlike the case of Thy-H₂O, they are not negligible) and similar for all the Thy-(H₂O)₂ clusters.

In the A and D case, water acts as a hydrogen acceptor, whereas for E it is the hydrogen donor. We see the expected behaviour in the resonances: stabilization for E and destabilization for A and D. In addition, the figure also shows that which of the thymine atoms the water molecule binds to has a small effect on how much the resonances is stabilized/destabilized: small differences are visible in the resonances for A and D (as was also the case for Aeq and Deq in the previous section). Looking at the results for the AD and AE clusters we can see that the effect of water on the thymine resonances is approximately

additive (the shift does not always add quantitatively). We can also see that the stabilization/destabilization effect can be reduced or even cancelled out if one water is a donor and another an acceptor. An example is the second resonance for the AE cluster in Figure 5.

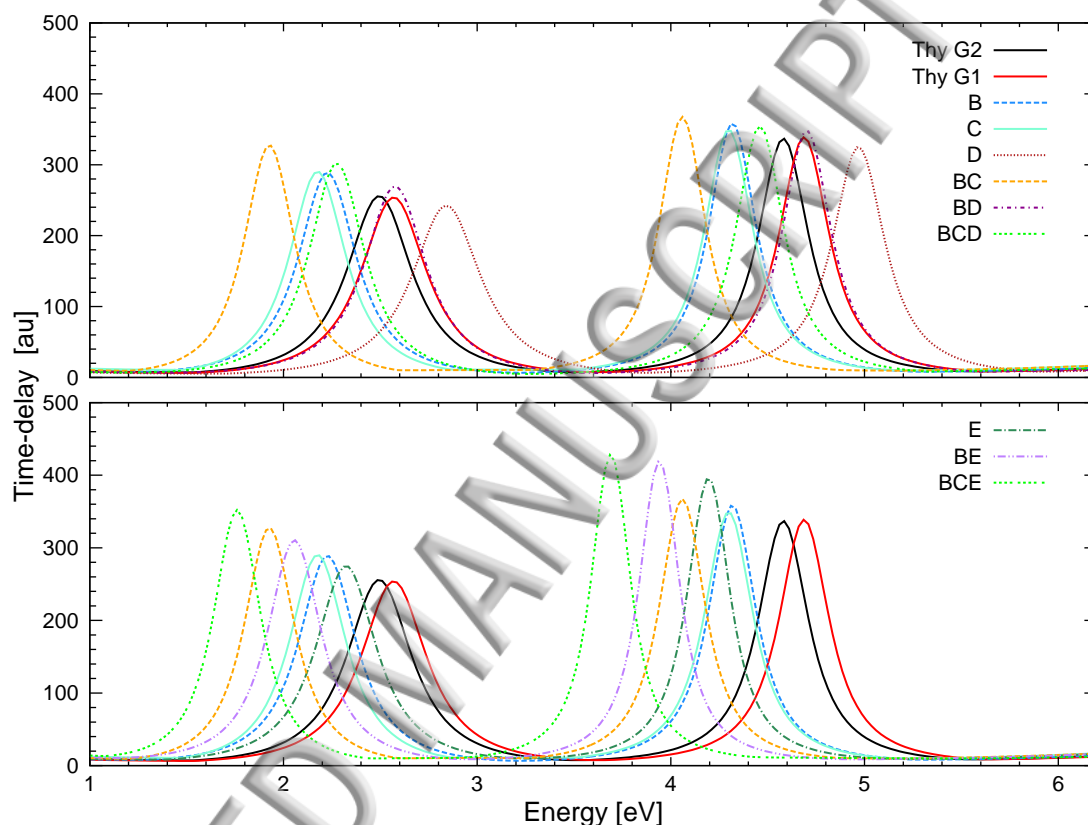


FIG. 6: Time-delay calculated at SE level with 10 v.o. for: thymine in its equilibrium geometry (Thy G1), the geometry it has in the ABCDE cluster (Thy G2), and Thy-(H₂O)_n, $n = 1, 2, 3$ for the geometries indicated in the panels. The time-delay for Thy G2 and clusters B, C and BC is plotted in both panels; the legend in the lower panel applies to both.

Figure 6 shows the time-delays for two Thy-(H₂O)₃ clusters. This Figure confirms that the conclusions obtained looking at Thy-(H₂O)₂ also apply to the clusters with three water molecules. Specifically, the effect of water on the thymine resonances is approximately additive.

Thymine-(H₂O)₅

The effects of microhydration for the two different Thy-(H₂O)₅ clusters presented in Figure 1 can be investigated by analyzing Figure 7, where their time-delays are shown. Comparison of these, the time-delay for isolated thymine in its gas phase equilibrium geometry and those for the geometry thymine has in each cluster (Thy G2 and Thy G3) will elucidate the direct and indirect effects.

The geometry of thymine in clusters ABCDE and ACDEF are slightly different, and this is reflected by the fact that the positions of the resonances for Thy G2 and Thy G3 in Figure 7 are visibly different. As can be observed, the resonances for Thy G2 are closer to those of isolated thymine, because the geometry is more similar to it than Thy G3. The indirect effects are stronger for the ACDEF cluster. For each cluster, the stabilization is similar for both resonances.

The comparison of the resonance position for the clusters and thymine in the geometry it has in each of them (Thy G2 and Thy G3) allows us to quantify the direct effect. We can see that for both clusters the lowest resonances is slightly destabilized whereas the second resonance is stabilized by the direct effects. The influence of the direct effect on the second resonance is stronger than for the first resonance (and this can, once again, be explained looking at the LUMO and LUMO+2 orbitals). Finally, direct effects are stronger in the ACDEF cluster than in the ABCDE one, and this is particularly obvious in the case of the second resonance.

The difference in the size of the shift for the first π^* resonance between the two clusters can also be understood by comparing the LUMO and LUMO+2 orbitals. In the ABCDE cluster two of the water molecules which act as a hydrogen donor are close to the electronic density associated to the first π^* orbital, whereas for the cluster ACDEF this is the case for only one water molecule. Therefore the overall effect on the first π^* resonance of the ACDEF cluster is destabilization, while the position of this resonance of cluster ABCDE hardly changes. The differences in the second π^* resonance shift between the two clusters is harder to explain by looking at LUMO+2 orbital, since the same number of water molecules which are hydrogen donors are close to the second π^* orbital. Therefore, the reasons might be linked to the distance between thymine and water (i.e. a stronger hydrogen bond in the ACDEF cluster).

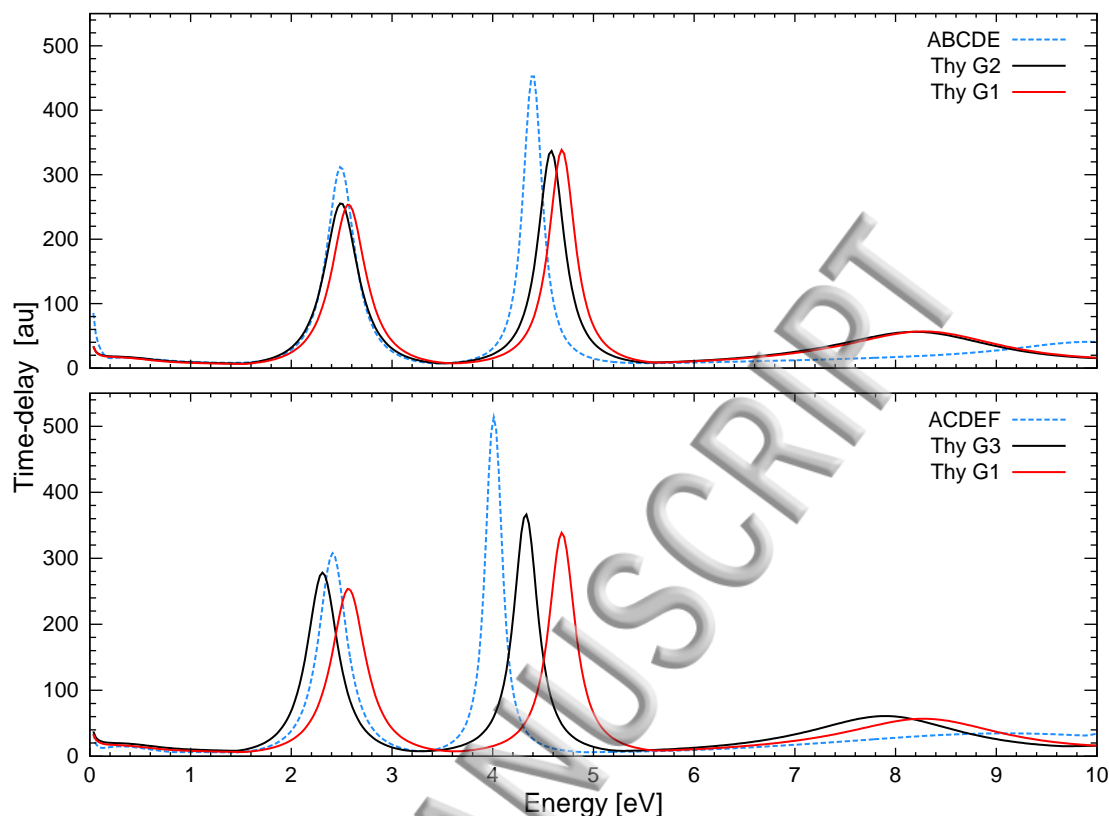


FIG. 7: Time-delay for Thy-(H₂O)₅ for the two geometries discussed in the paper and isolated thymine in its equilibrium geometry (Thy G1) and that it has in the ABCDE and ACDEF clusters (Thy G2 and Thy G3 respectively). Calculations performed at SE level with 10 v.o.

To analyse the total effect of water on the resonances of Thy-(H₂O)₅ we compare the time-delay for Thy G1 with that for each cluster. The first and second resonances are stabilized for both clusters (the same is the case for the SEP calculations) although not the same amount: the lower resonance is hardly stabilized (in particular for the ABCDE cluster) whereas the higher resonance is stabilized by almost 0.7 eV for the ACDEF cluster. (We note that the third π^* resonance seems to be destabilized for both targets. However, since this resonance is of mixed shape core-excited character, the SE approximation describes it very poorly; in fact, some test SEP calculations would seem to indicate that this resonance is also stabilized when a more sophisticated description of the system is employed).

The total effect of microhydration is stronger for the resonances of the ACDEF than the ABCDE cluster. This can only be partly ascribed to the stronger indirect effect in the ACDEF cluster: the direct effects are also stronger for the ACDEF cluster for the reasons

explained above. The changes in the resonance position (due to the total effect) in the two clusters are not large. Only the second resonance of the ACDEF cluster shifts more than 0.5 eV towards lower energies. The resonance shifts of both clusters are approximately equal to the energy differences of the π^* orbitals of the clusters with respect to isolated Thy G1 (the same was observed for pyridine in Paper I). We note that SE and SEP results (the latter have not been included in this paper) give qualitatively the same picture of the water influence on resonance de/stabilization. The SEP results, however, lead to bigger shifts. This, however, is not the case for all clusters studied in this work: occasionally the shift in the SE calculation is bigger than in the SEP one.

We conclude that the role of indirect and direct effects on the resonance positions for Thy-(H₂O)₅ is not always the same: one can be stabilizing while the other one is destabilizing. In the cluster for the optimized geometry, the indirect effects are smaller than the direct ones, as the case for the Thy-(H₂O)_n cluster for $n \leq 3$ and for the pyridine clusters investigated in Paper I. Moreover, even though the total effect leads to the stabilization of both resonances, the effect is not quantitatively always the same. Even two resonances of similar characteristics as the two we have focused on in this work behave somewhat differently.

Our SEP results for resonance shifts for these systems are not particularly reliable for two reasons: (i) as indicated in Paper I, we are unable to control or determine how much of the polarization we are describing so may be including different amounts for cluster and isolated target; (ii) given the size of the calculation for Thy-(H₂O)₅, we could only include a small number of virtual orbitals that almost certainly describes a small part of the polarization effects. However, the picture we obtained when including 30 v.o. for Thy-(H₂O)₅ and 20 v.o. for isolated thymine (Paper I explains how we choose these numbers) is similar to that obtained from the SE calculations although in the SEP case the shifts are more similar. Attempts at using polarized orbitals obtained from a PCM calculation (using the cc-PVDZ basis set) in the SE scattering calculations lead to very similar results: the lower π^* resonance is slightly less stabilized whereas the higher one is somewhat more stabilized. The result is consistent with our conclusion (from both SE and SEP calculations) that the second resonance is stabilized more by microhydration).

Discussion

We turn now to a discussion of previous studies of DEA to microhydrated thymine/uracil.

Gallup and Fabrikant³² determined that attachment to a very wide σ^* resonance (and vibrational Feshbach resonances linked to a dipole bound state that interacts with this resonance¹³) leads to N₁-H fragmentation and that H loss from the N₃ site is due to vibronic coupling between a σ^* (A') and the second π^* (A'') resonances (the electron initially attaches to the π^* resonance). The former mechanism contributes to the H detachment at lower energies and the latter at higher energies³⁶. Smyth *et al.*³¹ performed 1-dimensional calculation for H detachment in thymine/uracil from N₁. The cross section showed a strong enhancement that they attributed to two effects: lowering of the resonance position of thymine/uracil (stabilization) and the increase of the resonance lifetime, both due to interaction with the water molecules. As stated in the introduction, the stabilization of the resonance was determined by calculating the VEA of the first π^* resonance using bound state techniques. The changes to the resonances width were determined from multiple-scattering calculations.

Our results confirm that the π^* resonances are stabilized, but indicate that the assumption that all resonances are affected in the same way by microsolvation may be incorrect (the very wide σ^* resonance does not appear in our calculations, as is always the case for these type of resonances²³, nor is there clear evidence for another shape σ^* resonance in the appropriate energy range). Approximate inclusion of polarization effects seems to indicate (see below) this is unlikely to change if polarization is accurately included in the calculation, unless: (i) this inclusion increases the shifts so significantly as to make the contribution of the static potential irrelevant or (ii) the contribution is significantly different for different resonances. Smyth *et al.* estimate a shift of around 0.3 eV for the first resonance for the ABCDE cluster, whereas we estimate 0.075 and 0.29 eV for the first and second resonance respectively. The latter value would seem inconsistent with an inordinate contribution from polarization effects to the shift.

The strongly enhanced cross section for the fragmentation process obtained by Smyth *et al.* seems in contradiction with the results of the experiment carried out by Kočíšek *et al.*³³ However, three issues might partially explain this inconsistency:

- Thy-(H₂O)₅ may not be a good model for the majority of clusters present in the experiment. The experimental set-up does not allow to determine or select the pro-

portion of clusters of different sizes (i.e. with different numbers of water molecules). The expectation is that the clusters are relatively small (i.e. contain a small number of water molecules), particularly for lower hydration conditions.³³

- The calculations only investigate one of the mechanisms of H loss (that linked to the N₁ site) and make no prediction about how detachment from the N₃ site would be affected.
- The calculations do not account for 'caging' effects that can prevent the H from leaving the proximity of the thymine molecule.

In their SE calculations for singly and doubly hydrated phenol, de Oliveira *et al.*³⁵ find that both π^* resonances in phenol are generally stabilized (the higher energy one more so than the lower one) for the complexes they study. However, they suggest that dihydrogenation in phenol could be severely impeded by microhydration. Hydrogen elimination in this molecule occurs from the OH group and proceeds via vibronic coupling between the second π^* resonance and a shape resonance associated to a σ^* orbital located along the OH bond³⁷. The authors note that, for isolated phenol, this orbital corresponds to the LUMO+2 whereas, for three out of the four microhydrated phenol geometries studied, the LUMO+2 orbital corresponds to electronic density localized mainly around the water molecules. They propose that the vibronic coupling would therefore no longer lead to phenol dehydrogenation. A similar σ^* - π^* coupling is responsible for H detachment from the N₃ site (with the σ^* orbital along the NH bond). In this case, the orbitals involved are LUMO+2 (second π^*) and LUMO+4 (σ^*) (these and other orbitals mentioned are plotted in the Supplementary Material). We observe that, in the cluster, the energy of these orbitals changes and those of σ^* character have significant density on the water molecules. This is true for the LUMO+4 (that actually becomes LUMO+5) but also for the first σ^* orbital, the LUMO+1. Therefore, a similar effect might be responsible for the quenching of the anion yield due to detachment from the N₃ nitrogen. What is more, the fact that there seems to be no low-lying orbital in Thy-(H₂O)₅ with significant electronic density around the N₁H bond might also explain changes to the H loss from N₁.

IV. CONCLUSIONS

The effect of microhydration on thymine has been investigated. As already established^{26,35,38} and in agreement with results for pyridine in Paper I, the resonances of thymine are stabilized when water is a donor in the hydrogen bonding and destabilized when water is the acceptor. In some of the Thy-H₂O clusters studied here, however, a water molecule formed two bonds with thymine, being therefore donor and acceptor at the same time. In those cases, at SE level, the lower π^* resonance was slightly destabilized whereas the higher energy one was stabilized.

Calculations for Thy-(H₂O)₂ and Thy-(H₂O)₃ have shown, as expected, that the effect of water is approximately additive. Unlike the case of pyridine (see Paper I) there is no straightforward correlation between the dipole moment of the cluster and the amount of stabilization of the resonances (nor was there correlation for the formic acid-water clusters²⁶ or phenol-water clusters³⁵). This seems reasonable on account of the fact that, in the thymine clusters, additional water molecules attach to the thymine molecule (rather than themselves) and therefore tend to surround the ring.

Our results show that the effect of microhydration on resonance positions can be different for different resonances in the cluster. At SE level, where only the effect of the static and exchange potentials is modelled, it is even possible for one of the resonances to be destabilized when the other one is stabilized. We believe the small stabilization of both π^* resonances in Thy-(H₂O)₅ is not inconsistent with the experimental results of Kočíšek *et al.*³³: if these results were used in calculations of the type carried out by Smyth *et al.* they would probably lead to an enhancement of the H detachment cross section. However, as explained in the Discussion, other effects may be playing a significant role. For example, our calculations for other clusters (even if these were not all for optimized geometries) show mostly small stabilizations or even destabilizations. Although it is not possible to tell the composition of the cluster gas in the experiment (it is possible, though perhaps not likely, that most of the Thy-(H₂O)_n clusters are for $n > 5$) these results seem consistent with either little effect due to microhydration or even a reduction in DEA. More interestingly, the amount of stabilization/destabilization of the two lowest π^* resonances at SE level is similar to the change in the HF orbital energies involved in these resonances. The σ^* resonances proposed to be involved in the H loss mechanisms are not visible in our calculations. However,

the corresponding σ^* orbitals change so significantly as to no longer describe electronic density around the N_1 or N_3 bonds. It is therefore possible that the quenching observed experimentally is linked to significant modification of the σ^* rather than π^* resonances of thymine. Further calculations and, ideally, experiments with selected clusters would help elucidate the quenching effect.

V. SUPPLEMENTARY MATERIAL

Plots of the most relevant Hartree-Fock orbitals (from HOMO-5 to LUMO+6) for Thy G2, and Thy-(H₂O)₅ in the ABCDE geometry are presented in the supplementary material. Also presented are some representative elastic cross sections for Thy-H₂O and Thy-(H₂O)₅ clusters.

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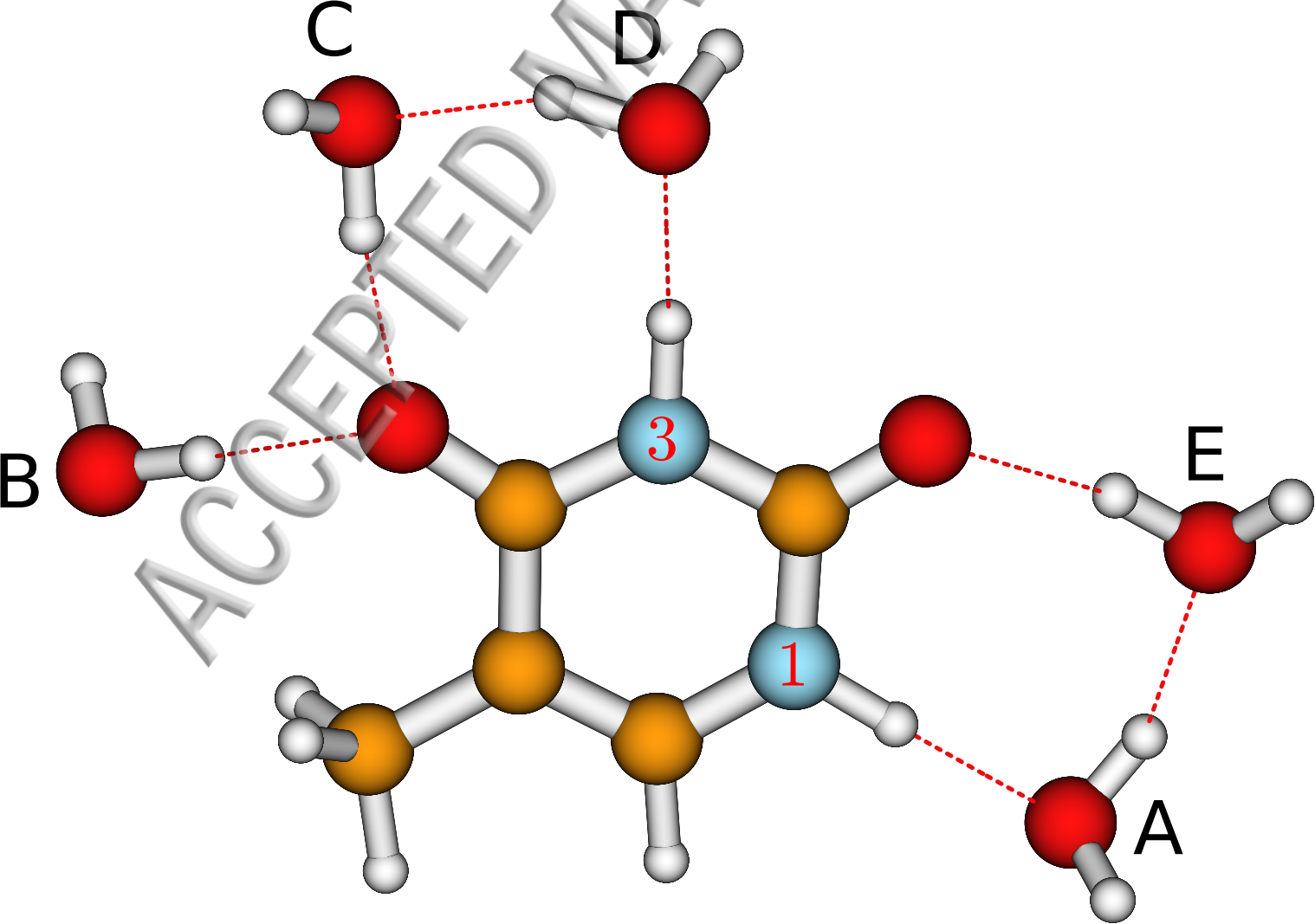
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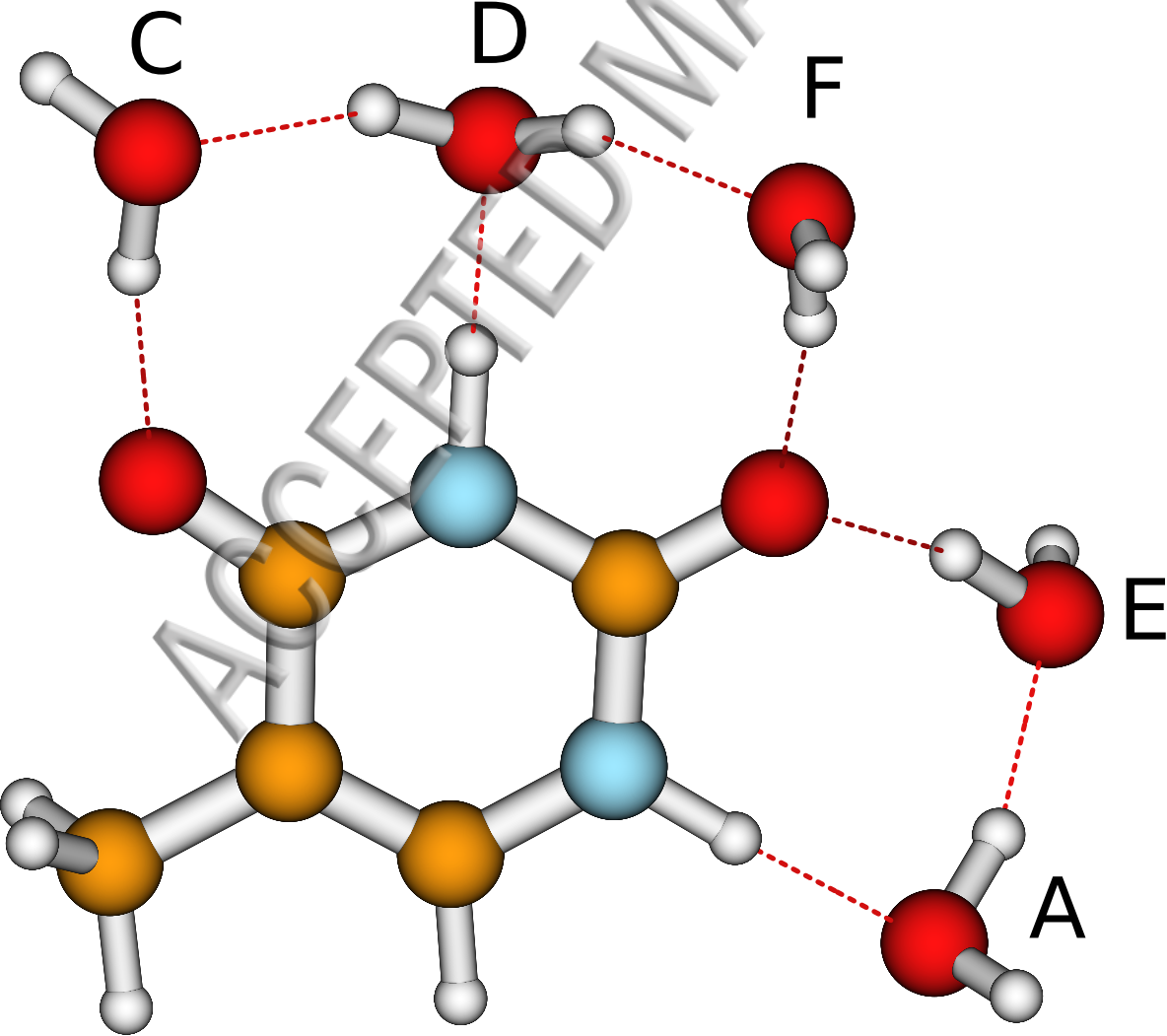
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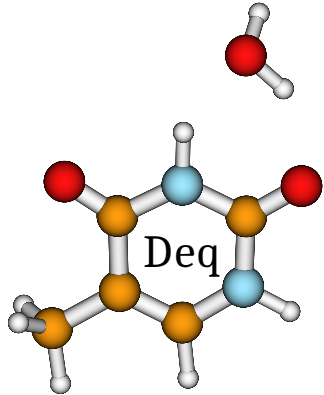
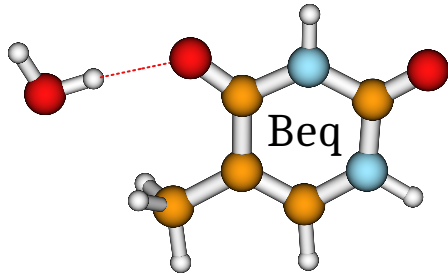
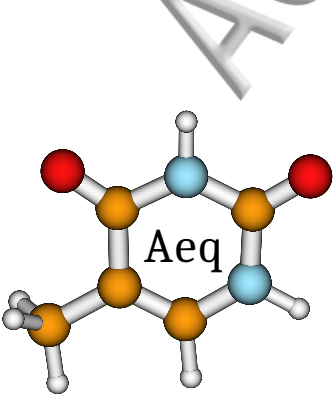
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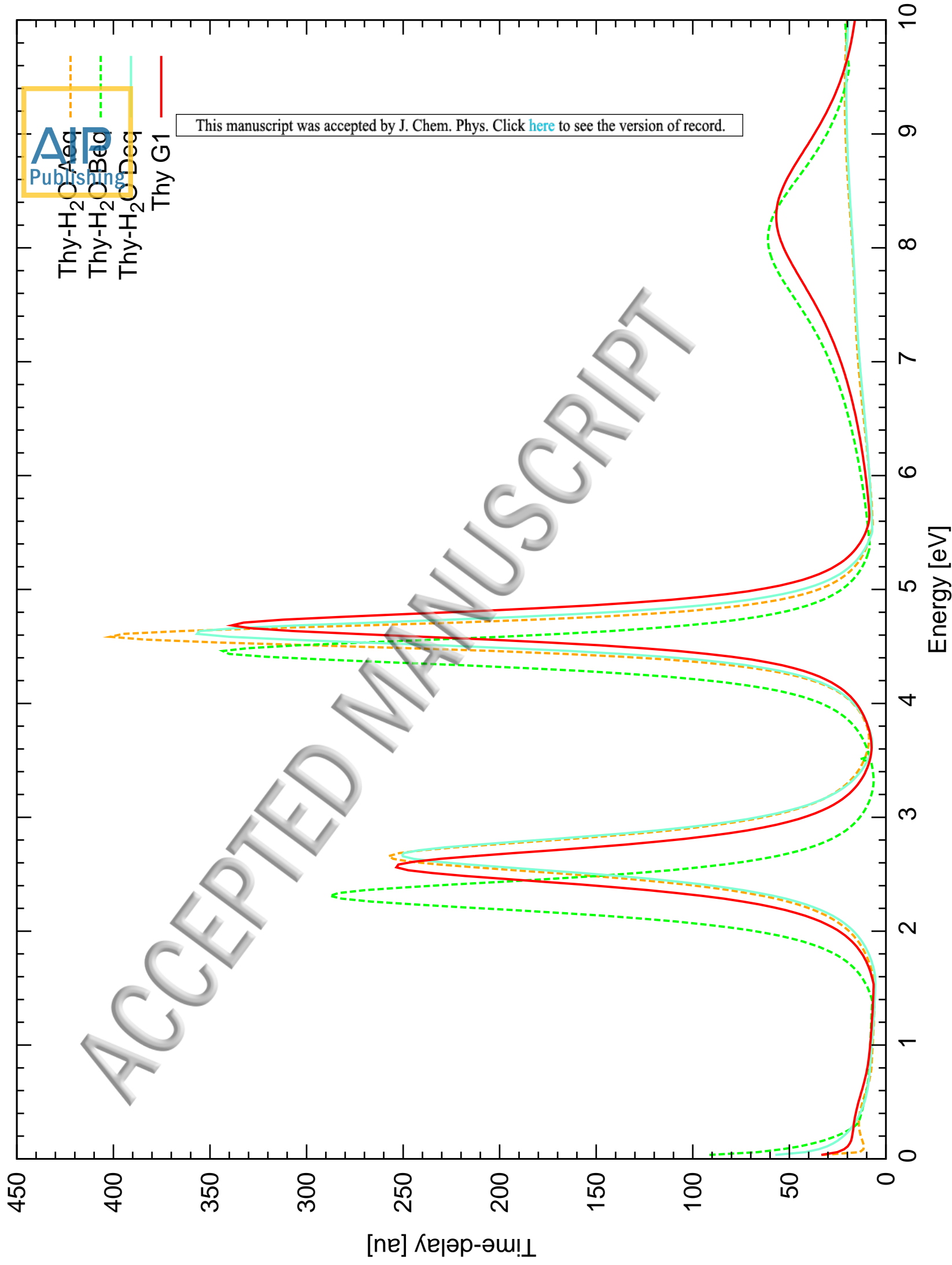
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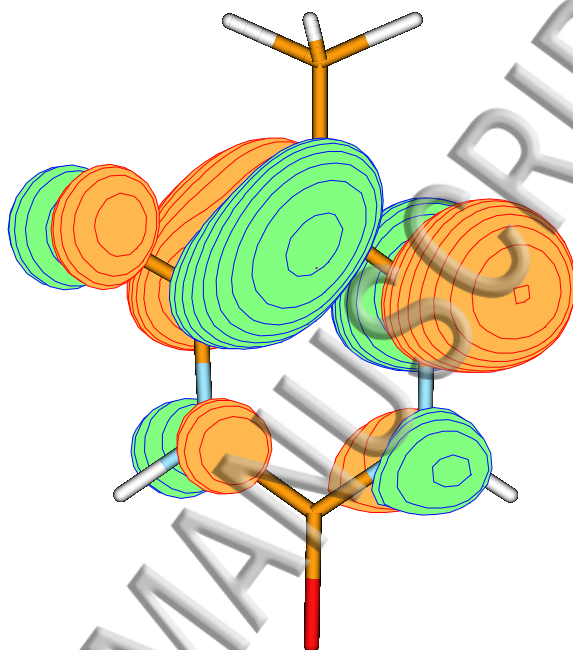
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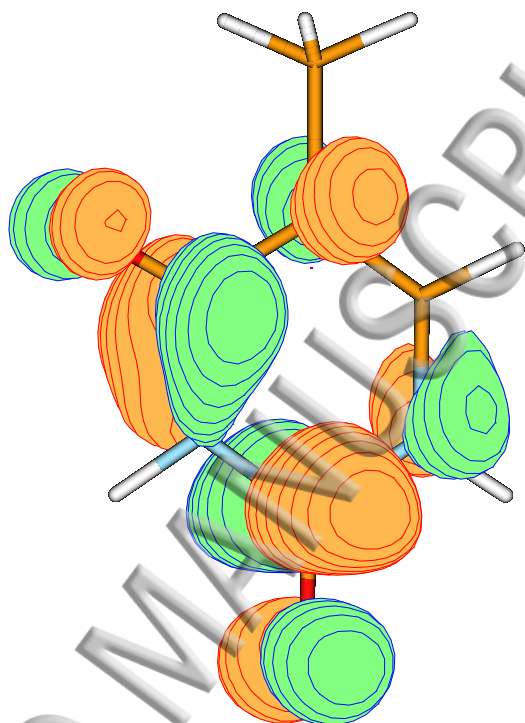




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